Graphitized Carbon Black in Quartz Tubes for the Sampling of Indoor Air Nicotine and Analysis by Microwave Thermal Desorption–Capillary Gas Chromatography

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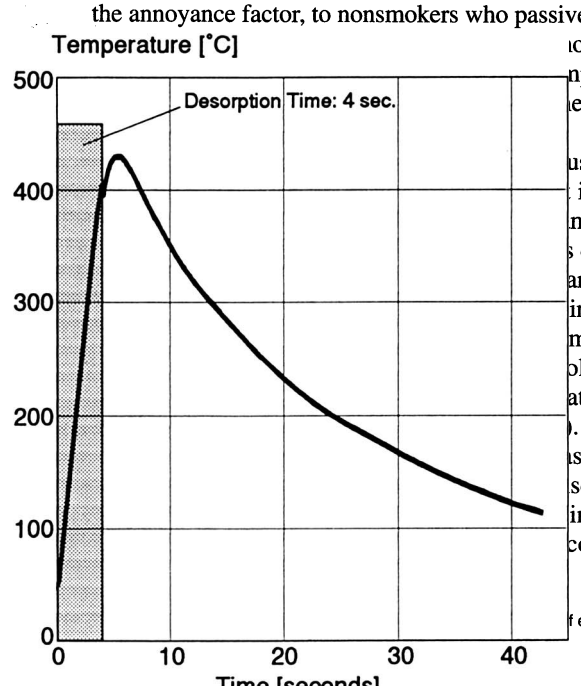
Abstract

Nicotine in a smoky indoor air environment can be determined using graphitized carbon black as a solid sorbent in quartz tubes. The temperature stability, high purity, and heat absorption characteristics of the sorbent, as well as the permeability of the quartz tubes to microwaves, enable the thermal desorption by means of microwaves after active sampling. Permeation and dynamic dilution procedures for the generation of nicotine in the vapor phase at low and high concentrations are used to evaluate the performances of the sampler. Tube preparation is described and the microwave desorption temperature is measured. Breakthrough volume is determined to allow sampling at 0.1–1 L/min for definite periods of time. The procedure is tested for the determination of gas and paticulate phase nicotine in sidestream smoke produced in an experimental chamber.

Introduction

Sidestream tobacco smoke, which is emitted from the burning end of a cigarette between puffs, is known as one of the major sources of indoor air pollution (1). The health effects, as well as the annoyance factor, to nonsmokers who passively inhale envi-



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suspended particulate matter from the air on filters with the aid of pumps (5,6). Condensed nicotine is reported to be captured by the use of an open-face glass Petri dish placed on the cooling surface of a thermoelectric cold plate (7,8), but the method suffers limitations (9). Hammond et al. (10) described a treated filter method which allowed the combined sampling of particulate and gaseous nicotine. In these procedures, gas chromatography is used to separate and analyze nicotine after liquid extraction of the filter by an adequate solvent and liquid injections of the extract. The gas phase nicotine can also be collected with a passive sampler or a diffusive denuder (11,12).

Muramatsu et al. (13,14) were the first to report a nicotine analytical technique based on a sampler tube filled with Uniport-S coated with 10% silicon polymer OV-17. The tubes are thermally desorbed onto a GC column. They needed ammonia vapor added to the carrier gas to effectively desorb nicotine because of the acidic property of the treated sorbent. Improvement of this method was described by Thompson et al. (15) and recently published techniques made use of Tenax as adsorption material (16,17). An interesting paper dealing with the latest techniques in use and with an intercomparison of sampling devices for indoor air nicotine has been published recently (18). Our paper reports the use of a new adsorbent material for the sampling and a different thermal desorption principle for the determination of ambient air nicotine. The method was validated by generating nicotine in the vapor phase and also by sampling sidestream tobacco smoke in an experimental chamber.

Experimental

Preparation of Carbotrap tubes. Transparent quartz tubes (Quartz & Silice, Les Miroirs, Défense 3, Paris, France) were cleaned in a boiling mixture of concentrated nitric and hydrochloric acids (1:1 v/v) for 15 min, then rinsed with demineralized water and dried at 120°C. The tubes were silanized using a solution of 10% dimethyldichlorosilane in toluene and left to react for 1 h. After rinsing with toluene and methanol, they were dried in an oven. Each tube was filled with 70 mg of Carbotrap graphitized carbon black, 20/40 mesh (Supelco 2-0287), and plugged with silanized quartz wool at the two ends (Figure 1). Prior to sampling, blank tubes were conditioned by thermally

desorbing any adsorbed trace contaminants three times for 10 s each. During this operation, the GC column was disconnected from the interface. Tubes were capped with plastic stoppers and stored in closed vials in preparation for sampling operations.

Microwave thermal desorption and GC conditions. The MW-1 microwave desorber (Rektorik, Geneva, Switzerland) was coupled to a Varian GC Model 3400 equipped with a thermionic nitrogen specific detector (NPD) and capillary column. A slight modification was made to the gas system in the desorber. A syringe needle (SGE, Model 100-500 AN5) was mounted at the outlet of the desorber. The bypass, backflushing, and split system of the desorber were discarded and the gaseous effluent was guided directly into the injector of the GC, which was set in the split mode (Figure 2). Desorption conditions were as follows: interface temperature, 200°C; desorption time, 4 s; desorption power, "Low." The heat temperature transferred by the microwaves to the tube was measured with the probe of a Cr–Alumel thermocouple introduced in the sorbent bed.

The 25-m × 0.25-mm i.d. WCOT fused-silica capillary column, coated with a 0.25-µm film of CP-Sil-5CB (Chrompack) was used for the separation. GC conditions are as follows: injector temperature, 250°C; oven temperature, 120°C isothermal; split mode, 1.5:10; carrier gas, nitrogen with the manometer pressure set at 14 psi. The NPD was supplied with 4 mL/min hydrogen, 30 mL/min nitrogen (as the makeup gas), and 175-mL/min air, and was maintained at 280°C.

Generation of vapor phase nicotine. To test the performances of the Carbotrap tubes, as well as the overall analytical procedure, nicotine was generated in the vapor phase by the permeation process (19) for the low concentration range (< 1 µg/L). A weighed amount of pure nicotine was contained in a small, open glass ampule connected to short silicone tubing and stoppered with a glass stopper. The liquid nicotine should not moisten the piece of silicone. The permeation device was placed in a temperature-controlled permeation calibration apparatus equipped with gas inlet orifices (Metronics Dynacalibrators, Model 450). Nicotine diffused through the silicone surface, was flushed with nitrogen, and finally diluted with purified air before sampling. For higher concentrations of nicotine in air (ca 50 µg/L), a dynamic generation procedure was used. A measured amount of nicotine was slowly delivered by a Hamilton µL syringe pushed by a step motor into a heated flask. The flask temperature was controlled between 50 and 80°C depending on the desired concentration of nicotine. Vaporized nicotine was first diluted with nitrogen in the flask, then flushed with air through a multiorifice ampule where simultaneous samplings could be carried out. The Carbotrap tube was connected for 10 min to a personal pump (20) that aspirated the air at a flow rate of 0.1 L/min. The tube was ready for desorption with the MW-1 microwave desorber.

Desorption efficiency and calibration with standard vapor phase nicotine. A primary calibration curve was first constructed from standard solutions containing known amounts of nicotine (> 97%, d:1.008, Fluka 72290) in methanol by liquid injections in the GC with the desorber disconnected. The concentration of nicotine in gaseous effluents can be calculated from the generation systems, provided the weight or volume of nicotine delivered by the syringe, the flow rates of dilution gas, and other parameters are under control. The stability of the generation process was assessed by multiple samplings over time at each concentration. The quantities of nicotine in the tubes were calculated from the concentration in air and the volume of air sampled. This amount of vapor-phase nicotine sampled with Carbotrap tubes and generated under defined conditions was then experimentally determined according to the thermal desorption procedure. The areas of the respective GC peaks were then plotted versus the calculated values of nicotine, giving a vapor phase cal-

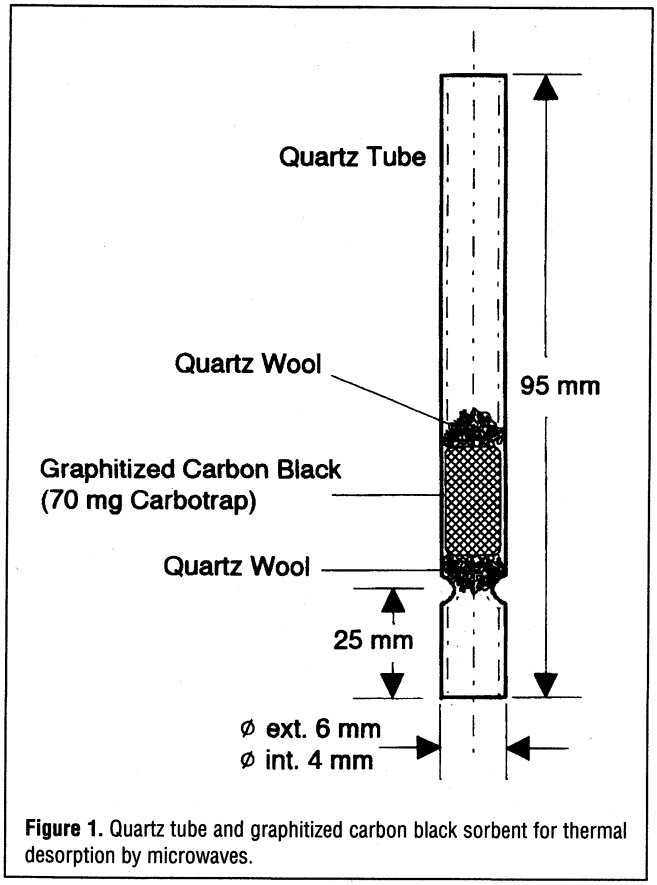

Figure 1. Quartz tube and graphitized carbon black sorbent for thermal desorption by microwaves.

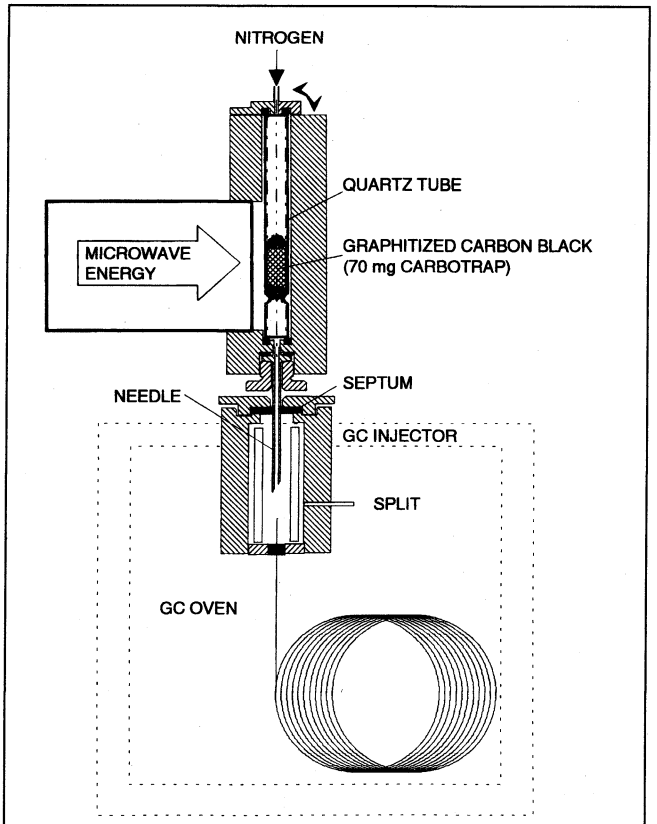

Figure 2. Schematic diagram of the sample introduction.

ibration curve. An amount of nicotine corresponds to each of these areas from interpolations on the primary calibration curve. The amount of nicotine derived from the vapor phase calibration and the value associated with the liquid injections of standard were plotted using the linear regression function for the correlation between both procedures.

Determination of the breakthrough volume V^t_g of the tube. Desired amounts of nicotine are sampled on several Carbotrap tubes. To determine the breakthrough volume, laboratory air is aspirated through a bottle containing active charcoal to remove organic impurities, then passes through the Carbotrap tubes for various definite periods of time. The breakthrough volumes are determined for flow rates of 0.1 and 1 L/min, respectively. The tubes are analyzed afterwards for their nicotine contents according to the outlined procedure. The resulting volume of air that passed through the tube is calculated for each flow rate. Average values of nicotine from four tubes not submitted to the passage of air represents the initial 100% level.

Sampling of nicotine in sidestream smoke in an experimental chamber with Carbotrap tubes; intermethod comparisons. The developed procedure was applied to the analysis of nicotine at various concentrations in sidestream tobacco smoke produced in an experimental chamber (21,22). Ambient air was drawn through Carbotrap tubes connected to personal sampling pumps operating at 0.1 L/min for definite periods of time between 15 min to several hours. The method of Hammond et al. (10) was used as a second method of sampling, simultaneously with the Carbotrap technique. Its principle is based on the liquid extraction of nicotine collected on a filter treated with sodium bisulfate.

On a few samples, the MW-1 desorber was directly coupled to the injector of a gas chromatography–mass spectrometry (GC–MS) system (Nermag R10-10) to verify that the nicotine peak is unique. The M^+ at *m/z* 162 was monitored as well as mass scans at the retention time of nicotine. The mass spectrum of nicotine in sidestream smoke was compared to that of reference standard nicotine injected under the same conditions.

Results and Discussion

Thermal desorption was presented as an effective means of sample introduction for GC analysis. The principles and characteristics of desorption technique by means of microwave energy have been described (23) and applications to the analysis of various volatile compounds were reported (24,25). The schematic diagram of the lab-made Carbotrap tubes and the modification of the sample introduction mounting are shown in Figure 2. The microwave thermal desorption of solid traps requires that the tube be made of quartz to be permeable to microwaves. At the temperature in this procedure, the quartz tube has a negligible reaction to the heating effect and very low thermal inertia for the transfer of the electromagnetic energy to the Carbotrap. Moreover, the quartz tube exhibits excellent thermal stability, high chemical inertia, and a high degree of purity. Ceramic tubes have been tested and showed good performance, but they are more porous and less inert.

The MW1 desorber was not equipped with a display of the desorption temperature. For a given power, the desorption time can be set from 1 to 10 s during which the electromagnetic energy is produced and transformed into thermal energy. The absence of information on temperature generated by microwaves is a major drawback. We solved the problem in calibrating a recorder scale and recorded the evolution of temperature in the desorption process. As seen in Figure 3, inertia is negligible and the temperature measured with the thermocouple reaches about 430°C in 4 s following a ballistic rise. The advantage of microwaves is that the temperature jump is instantaneous within seconds in contrast to other heat sources. A noticeable decomposition of nicotine was not observed.

Chromosorb 102 or Tenax GC absorb little microwave energy and heat cannot be transferred into the sorbents for the desorption of analytes, unlike using a classical thermal heating source. Commercial Carbotrap is a graphitized carbon black which has no ions or active functional groups on its homogeneous surface structure (26). Its hydrophobic character makes its performance unaffected by humidity. Although of high purity, the Carbotrap was heat-desorbed to remove any contaminant until a blank base line was obtained at the analysis conditions.

Independently of the necessities imposed by the use of microwaves as the heating source, Carbotrap sorbent can withstand a higher temperature to allow desorption of larger and high-boiling point molecules such as nicotine, in comparison with other polymeric sorbents. Tenax releases residues like toluene, benzene, and trichloroethylene (26) during thermal desorption, while XAD-2 completely pyrolyzes at 250°C. Solvent desorption of nicotine is possible at the expense of the method sensitivity. The Carbotrap sorbent and tube are reusable after adequate treatments and conditioning, although in this work the used sorbent was discarded. There is no particular difficulty in the preparation of the tubes. The use of 20/40 mesh size reduces the pressure drop, allowing the personal pump to operate without strain in the range of 0.1 to 1 L/min.

The retention capacity of the Carbotrap tube is dependent upon the sampling flow rate. The specific retention or breakthrough volume V^t_g of air needed to elute the adsorbate was determined for nicotine (Figure 4). At 1 L/min the sampling time is limited to about 6.6 h to maintain a 90% retention. For ambient nicotine

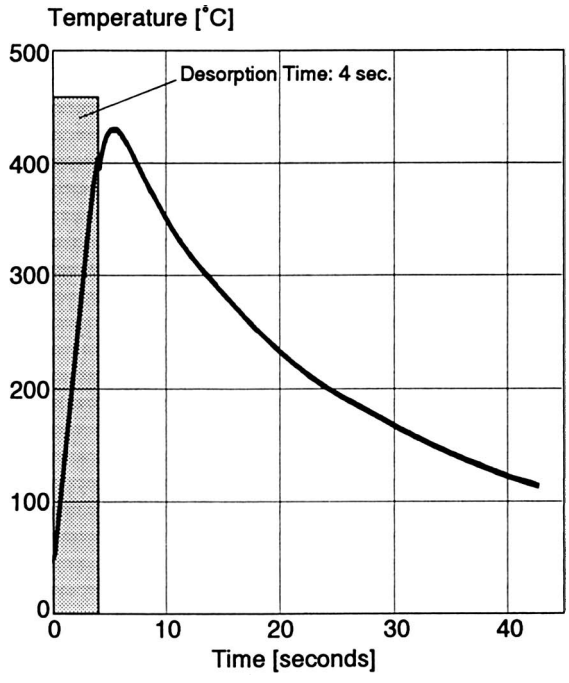

Figure 3. Measured temperatures transferred by microwaves to the sorbent bed.

sampled at 0.1 L/min, a sampling time as long as 166 h is permitted without loss of adsorption capacity for a 100% retention.

For the calculation of nicotine, it was logical to rely on a calibration curve constructed from thermally desorbed, known amounts of nicotine. Experiments carried out with 10 µL of standard solutions deposited on top of the tubes showed that the solvent elutes nicotine resulting in losses and nonreproducible results upon evaporation. The plot of a standard calibration curve cannot be made this way. The practice of quantitation of the thermally desorbed nicotine using a calibration curve constructed from liquid injections of known amounts of standard should be previously shown to be valid because the desorption efficiency was unknown. Calculation of the amount of nicotine using the vapor phase calibration curve and the curve derived from liquid injections of standard gave comparable results. This is illustrated in Figure 5, where the correlation function between the amounts of nicotine obtained from the thermal desorption using both the vapor phase and the liquid calibration curves shows a linear relationship with a slope close to 1 and a correlation coefficient R = 0.998. It can be stated that the desorption efficiency is quantitative over the concentration range and no irreversible adsorption is observed within the experimental errors of the method. On the other hand, the quantitation of nicotine by thermal desorption can be made relative to a liquid calibration curve constructed by injections of standard solutions of known concentrations, thus simplifying the use of the method.

Under the defined experimental conditions, the limit of detection of the method is 25 ng nicotine/tube (S/N = 10). Considering the low end concentration of 1 µg nicotine/m^3 in the indoor air, the method is applicable to a 4-h sampling time at 0.1 L/min or a 30-min period at 1 L/min. The limit of detection of methods based on liquid injections of the extract is higher, e.g. 2 µg for a 1-h sample (10), because only an aliquot of the final volume is injected. The method is characterized by its specificity due to the resolving power of capillary column chromatography with nitrogen selective detection, and also by its sensitivity, as the whole analyte is desorbed and introduced at once in the column. With the mounting shown in Figure 2, the desorption is not made in two stages as with cold trapping, and is therefore less time consuming, although this is accomplished at the expense of sensitivity, because injections are made in the split mode. It is still possible to obtain a lower limit of detection by cryofocusing the desorbed effluent. The overall elapsed time between two chromatographic runs is less than 20 min. Because thermal desorption is a one-shot analytical technique, it may be necessary to take care about the appropriate number of specimens to be sampled.

The second independent method was used to compare the results in the measurement of sidestream tobacco smoke generated in an experimental chamber, as neither are reference methods. The comparison is interesting because the two methods gave similar results, though they are based on different principles. Figure 6 shows the correlation (R = 0.993) between the two. This is relatively good, considering the global differences in the sampling and desorption processes. From the closeness of agreement, we conclude that total nicotine (gas and particulate) can be determined by the Carbotrap tube procedure.

As a check of peak specificity, the microwave desorber has been mounted on a GC–MS system and ambient nicotine in a few sample tubes was identified by its mass spectrum. Monitoring ion peaks at m/z 162 shows that no interference is present at the retention time of nicotine. The mass spectrum of nicotine in sidestream smoke and that of reference nicotine are similar. It can be anticipated that the technique of sampling by Carbotrap sorbent and desorption by microwaves developed for vapor and particulate nicotine in an indoor air environment is applicable to the desorption by a classical heating source.

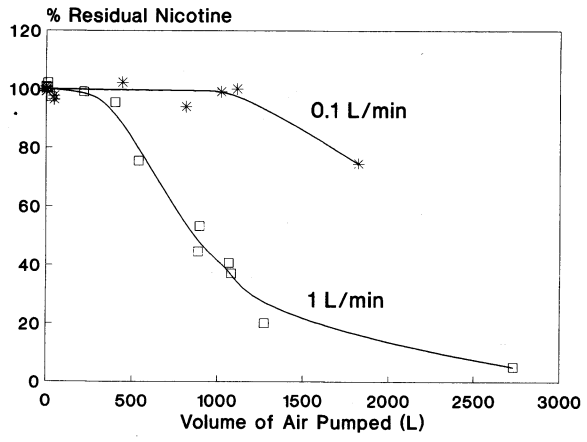

Figure 4. Determination of the breakthrough volume of the graphitized carbon black sorbent tube.

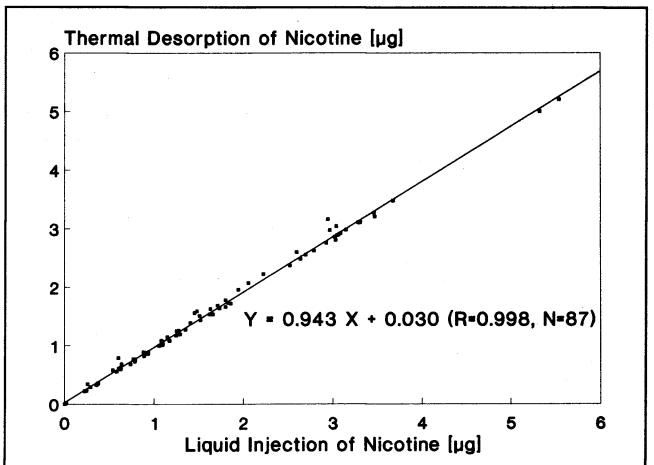

Figure 5. Correlation between the amount of desorbed nicotine and the known amount of standard solutions injected.

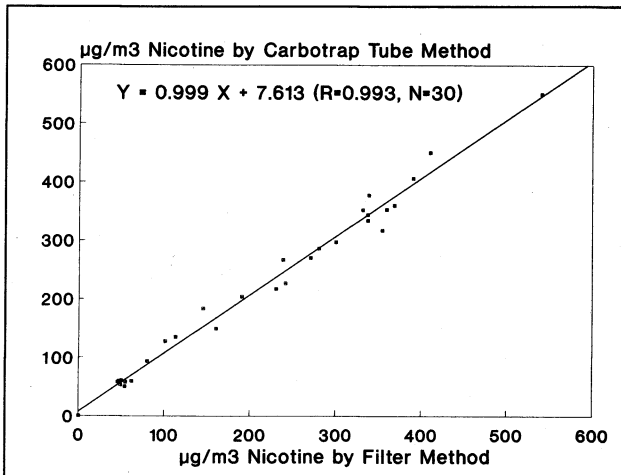

Figure 6. Nicotine in sidestream smoke determined by graphitized carbon black tube–microwave thermal desorption and by filter treated method (10).

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